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FLUORESCENCE TEST FOR URANIUM

BY

CLAUDE W. SILL AND H. E. PETERSON

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FLUORESCENCE TEST FOR URANIUM[1]

By Claude W. Sill[2] and H. E. Peterson[3]

INTRODUCTION

In the course of a series of investigations on vanadium deposits of the western United States, the Bureau of Mines collected many hundreds of samples for chemical analysis. As uranium is often associated with these vanadium minerals, they were also analyzed for uranium, which was found to be absent in a large percentage of the samples. Since the usual methods for determining uranium are laborious and time-consuming, it is very desirable to have some simple qualitative test that can be applied prior to a quantitative analysis to determine whether uranium is present or absent and thus save the time and expense of applying the quantitative analysis to the large proportion of samples containing no uranium. To be acceptable, the test should be specific for uranium, sensitive enough to detect small amounts of uranium, and simple enough to make it worthwhile to apply.

The available methods for detecting uranium lacked one or more of the desired characteristics. Eventually, however, a method was worked out that satisfied all the requirements. This method is probably more specific and sensitive than the usual qualitative methods for uranium, and its simplicity and speed of application make it ideal for testing samples prior to quantitative analysis.

It has been known for many years that hexavalent uranium salts fluoresce under the influence of ultraviolet light. It has also been known that solutions of uranium salts fluoresce under the proper conditions, although this fluorescence is usually described as being relatively weak (7). Fluorescence tests for uranium, therefore, have usually been made by bead tests (7). However, under certain conditions the intensity of fluorescence in aqueous solution is strong enough to find practical application in the analytical chemistry of uranium. The test described in this paper is the result of investigations carried out employing ultraviolet light for detecting uranium in aqueous solution. It is based on the greenish-yellow fluorescence produced when a solution containing hexavalent uranium is exposed to short-wave ultraviolet radiation. It was found that aqueous solutions of uranium are much more responsive to short-wave ultraviolet light than to long-wave ultraviolet light. Dement and Dake (5) report this to be true also for uranium minerals and compounds.

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Since uranium is most susceptible to short-wave ultraviolet light, the lamp used in this work was the Mineralight V-41 of the Ultraviolet Light Products Co., Los Angeles, Calif., which emits short-wave ultraviolet rays at 2,537 Ångstrom units. Tests were also made with the General Electric Red-Purple bulb B-H4, which transmits long-wave ultraviolet light distributed between 3,000 and 4,000 Ångstrom units, but these tests were so insensitive as to have little value.

The test described is sensitive enough to indicate amounts of uranium that would ordinarily be detected in the most precise chemical methods (4), but not so sensitive as to give positive tests with traces of uranium. This is a highly desirable feature, since all samples should be eliminated that do not contain determinable amounts of uranium. However, the method can easily be made to detect smaller amounts by proper selection of sample size and concentration. The test is highly specific and extremely simple in application. Moreover, it uses up none of the sample, so that if uranium is present, the solution examined may be carried on through the quantitative determination. The method was developed to precede a volumetric determination, using a 3-gram sample of low-grade ore in which the separated uranium is determined by titration with 0.025 N $K_2Cr_2O_7$. Since its development, the test has been used on hundreds of samples of various kinds and has been found satisfactory in all cases.

PROCEDURE

Weigh 3 grams of the low-grade ore into a 400-ml. beaker, and dissolve with HCl, HNO_3, and HF if necessary. Add 15 ml. of H_2SO_4, and take down to fumes of SO_3. Any dark coloration due to organic material is removed by dropwise addition of $HClO_4$ to the fuming solution. Fume off most of the free H_2SO_4, and cool. Dilute with water to 100 ml., and heat until all soluble salts are in solution. Filter, using a little paper pulp if necessary to give a clear filtrate, and dilute to 150-200 ml.

The fluorescence test is conducted in a dark room. The eyes of the analyst should be protected by plain, colorless glasses if he is to be exposed frequently or for periods of time longer than 15 minutes. 400-ml. Pyrex beakers, chosen for their low fluorescence, are used as containers for the solutions.

Place the clear solution on a dark, nonreflecting surface, and place the ultraviolet lamp on the open top of the beaker. In the presence of substances that absorb the radiation appreciably, which is the usual case, the uranium fluorescence will be noted as a bright greenish-yellow line immediately below the meniscus (fig. 1), if the eyes are at the same level as the meniscus and the solution is viewed at right angles to the incident beam. If the eyes are lower, it will be seen that the entire undersurface of the solution is greenish-yellow. This line, although narrow, is nevertheless very easily seen, due to the marked contrast with the body of the solution. In solutions that contain no substances that absorb this radiation appreciably, as, for example, water to which a very small amount of uranium has been added, the fluorescence is distributed more or less

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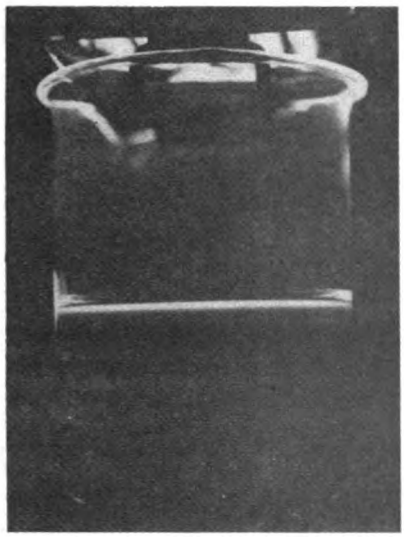

FIG. 1

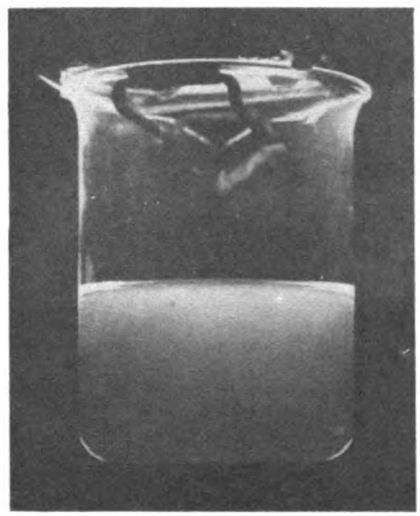

FIG. 2

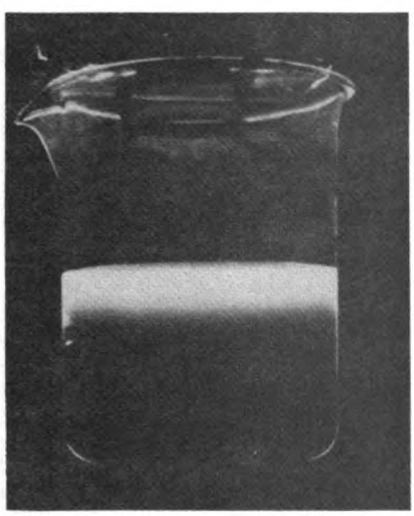

FIG. 3

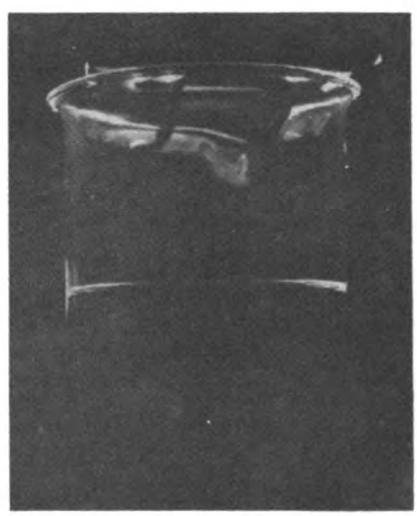

FIG. 4

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throughout the solution (fig. 2) and is of more greenish color than the line described above. As the uranium content is increased, the absorption of ultraviolet light is increased, resulting in less penetration of the light and a corresponding narrowing of the fluorescent band (fig. 3). With large amounts of uranium, the absorption is so strong that the ultraviolet light does not get much past the surface, and the absorption again appears as a line just below the meniscus. The contrast between the brilliant fluorescent line and the rest of the solution makes a decision as to the presence or absence of uranium very simple. Figure 4 shows plain water, with just the meniscus appearing.

Since certain substances desensitize and inhibit the fluorescence of uranium solutions, the following corroborating test should always be applied to establish definitely the presence or absence of uranium.

Test the solution under light as described. If no fluorescence is noted, uranium is not present, provided no inhibiting agent is present. Then add approximately 0.025 N solution of UO_2SO_4 dropwise to the solution under test, stirring the solution and testing for fluorescence after each few drops. If the fluorescence shows up after the addition of a few drops, the conditions for fluorescence were favorable, and since no fluorescence was noted before the uranium was added it is fairly certain that the original uranium content was not greater than the amount added.

Should the fluorescence fail to appear after several drops have been added, or if it should appear only very faintly after the addition of a fairly large amount of the uranium solution, it may be assumed either that some inhibiting agent is present or that the ultraviolet light is being absorbed too completely (ultraviolet light is absorbed partly by pure water). The appropriate separations must then be made to eliminate this difficulty before the test can be applied successfully. On the usual ores that are likely to contain uranium, such difficulties are rarely encountered, since the method of preparing the sample will eliminate most of the possible interfering substances. Samples containing large amounts of iron may offer some difficulty, especially if large samples are taken to detect small amounts of uranium, owing to high absorption of the light. In any event, the presence of any interference will be noticed if this test is applied and the analyst can then take the proper steps to eliminate the difficulty.

The above test also gives a measure of the sensitivity of the test on each particular sample, since it may vary, depending on the kind and amounts of ions present. In the usual type of low-grade uranium-vanadium ore, 2 to 3 drops of 0.025 N UO_2SO_4 solution in 200 ml. of solution can readily be seen. This would indicate a sensitivity of about 0.3 mg. of uranium at a dilution of 1 to 1,000,000. However, by reducing the 200 ml. volume, a much smaller amount of uranium can be detected.

INTERFERING ELEMENTS

Inhibitors:

There are several ions that inhibit the fluorescence of uranium solutions and at certain concentrations completely destroy it. Einecke

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and Harms (6) studied the effect of various ions on the fluorescence of uranium solutions. Their investigations were carried out with a quartz mercury vapor lamp emitting long-wave ultraviolet rays of 3,500 Angstrom units. Although their conditions were different, the results they obtained with long-wave ultraviolet light are very similar to those obtained with short-wave ultraviolet light.

The following ions were tested during this investigation and were found to have inhibiting properties: I^-, Br^-, SCN^-, $Cr_2O_7^=$, $Fe(CN)_6^{\equiv}$, $AsO_3^{\equiv}$, $S^=$, Cl^-, $HCOO^-$, NO_2^-, $S_2O_3^=$, Ag^+, VO^{++}, Fe^{++}, Tl^+, Tl^{+++}, $MoO_4^=$.

Noninhibitors:

The following ions have been tested and do not affect appreciably, if at all, the fluorescence of uranyl solutions: Na^+, K^+, Li^+, NH_4^+, Ca^{++}, Zn^{++}, Mg^{++}, Mn^{++}, Al^{+++}, Fe^{+++}, Cu^{++}, Cr^{+++}, Ni^{++}, Hg^{++}, Bi^{+++}, Cb^{+++++}, Ta^{+++++}, Ti^{++++}, Cd^{++}, Be^{++}, Sn^{++++}, ClO_3^-, BrO_3^-, IO_3^-, $SO_3^=$, $SO_4^=$, $PO_4^{\equiv}$, $AsO_4^{\equiv}$, Ac^-, VO_3^-, $Fe(CN)_6^{\equiv}$, $B_4O_7^=$, tartrate, citrate, and oxalate. The fluoride ion is quite remarkable in that, when present in moderate amounts, it causes a very pronounced increase in the intensity of the fluorescence. This fact may be of use where greater sensitivity is desired. Too large amounts of fluoride, however, result in complete destruction of the fluorescence. Also, certain cations, such as Li^+, Cd^{++}, and Be^{++}, enhance the the fluorescence, although to a smaller degree than the F^-.

Sn^{++++} ion does not interfere with the fluorescence. However, it may cause interference through the deposition of solid salts if the acidity is not high enough. Solid $Sn(SO_4)_2$ has a strong, golden-brown fluorescence and if allowed to precipitate will give the effect of a fluorescence in solution. In testing for uranium in the presence of Sn, the solution should be acidified strongly enough to prevent precipitation of basic tin salts. No interference with uranium results under these conditions.

Colored Ions:

It should be noted that visible color does not necessarily indicate absorption of ultraviolet light. Moderate amounts of Cu^{++}, Ni^{++}, and Cr^{+++} are without great effect, and Co^{++} can be tolerated in somewhat smaller degree. However, the latter ion is undesirable due to a masking effect of its color. Moderate amounts of HVO_3 do not interfere seriously, even when tested in solutions of low acidity (pH 5) where its visible color is most intense. To detect small amounts of uranium in the presence of very large amounts of HVO_3, however, the examination should be made very carefully, since HVO_3, like Fe^{+++}, absorbs light so strongly that large amounts may result in a very thin Fluorescent line. Amounts of $KmnO_4$ that give visibly transparent solutions will not interfere, but with larger amounts, the solution rapidly becomes opaque to the ultraviolet radiation. Although $Cr_2O_7^=$ has some inhibiting properties, it does not seem to interfere seriously in small amounts.

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Of the above-mentioned interfering substances, MnO_4^-, $Cr_2O_7^=$, $MoO_4^=$, Tl^{+++}, and Ag^+ should survive the initial treatment with fuming H_2SO_4 and $HClO_4$. The presence of the first two in amounts sufficient to produce interference is easily detected by their color. The interference of Cr_2O_7 and MnO_4 is easily eliminated by reduction, since neither Mn^{++} nor Cr^{+++} ions interfere, even in fairly large amounts. An excess of reductant may interfere, however, either because of its own inhibiting properties, that is, Fe^{++}, or by forming an inhibiting substance; that is, vanadium, which is so often associated with uranium, may be reduced to the blue VO^{++}. The most satisfactory method has been to reduce with H_2O_2 and eliminate the excess H_2O_2 by boiling. The boiling also insures complete reduction of the $Cr_2O_7^=$ and destroys the reddish-brown HVO_4 which is formed in the presence of vanadium and which interferes if present in large amounts. Small amounts of either MnO_4^- or $Cr_2O_7^=$, however, may be more conveniently reduced with a little $FeSO_4$, and the excess $FeSO_4$ oxidized by addition of $KMnO_4$ to a faint permanent pink. This slight excess of $KMnO_4$ does no harm. This method is inadvisable on other than small amounts, since it tends to increase the concentration of Fe^{+++}, which absorbs the ultraviolet light strongly. Small amounts of MnO_4^- may be reduced conveniently by slow, dropwise addition of $NaNO_2$; a small excess of $NaNO_2$ is not objectionable, and too great an excess can be destroyed by the addition of a small amount of urea. In samples containing incompletely decomposed organic matter, the HVO_3 may have become reduced. In such a case, the vanadium should be reoxidized with $KMnO_4$ and the excess destroyed with $NaNO_2$ as described above.

If the test indicates that excessive amounts of either Fe^{+++} or the more highly colored ions are present, a separation must be made before the test can be applied successfully. A satisfactory separation may be made as follows: Solid Na_2CO_3 is added to the acid solution until neutral, and then an excess of 1 to 2 grams is added. The solution is boiled for about 15 minutes and filtered hot. The filtrate is acidified, boiled to expel CO_2, and the test applied.

The separations of Ag^+, Tl^{+++}, and $MoO_4^=$ have not been found sufficiently complete to prevent some interference from these sources. However, these ions are so rarely encountered in uranium ores that more complete removal has not been investigated.

DISCUSSION

This test has been applied to other problems besides the one for which it was originally developed. It has been used to detect uranium in columbium-tantalum ores after decomposing the ore by pyrosulfate fusion and leaching with dilute H_2SO_4. It has been most helpful in checking separations employed in the conventional quantitative schemes of analysis. For instance, the precipitation of uranium as $UO_2NH_4PO_4$ from buffered acetate solution has not produced entirely satisfactory results. Examination of the filtrate from this separation almost always shows the presence of variable amounts of uranium. These amounts are usually small and may be unimportant in the usual macro-determinations, but for semimicro work on low-grade materials, they may cause quite serious error. The loss occurs in the

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analysis of actual ore samples, although there is no difficulty in separating uranium completely from pure solutions of uranium. A Na_2CO_3 separation is used to remove iron prior to the precipitation of the uranium, and it may be that incomplete precipitation is caused by failure to eliminate CO_2 completely. Further work is being done on this point. Other applications have been found in studying the amount of uranium occluded by $Fe(OH)_3$ and the retention of $UO_2NH_4PO_4$ in the pores of filter paper.

CONCLUSION

The fluorescence test for uranium described in this paper has been tried for over 2 years on various types of samples with very reliable results. It is more specific and sensitive than the usual qualitative methods for uranium, and its simplicity and speed of application contribute greatly to its usefulness.

Samples submitted for uranium analysis can be tested at the outset for uranium. Those containing no uranium can be eliminated, thereby effecting a large saving in time and expense. The test has the advantage of using up none of the sample; it is an integral part of the quantitative scheme of analysis, so if uranium is found, the analyst can continue on with the quantitative determination.

There are very few interfering elements that are not removed in the preparation and solution of the sample; those that do remain, with the exception of Ag^+, Tl^{+++}, and $MoO_4^=$ ions, can easily be eliminated.

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